View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by The University of Utah: J. Willard Marriott Digital Library

Linear And Nonlinear Optical Spectroscopies Of PPE/PPV Copolymer Semiconductors

M. H. Tong[a], Z. V. Vardeny[a] and Y. Pang[b]

[a]*Department of Physics, University of Utah, Salt Lake City, Utah 84112-0830*
[b]*Department of Chemistry & Center for High Performance Polymers and Composites, Clark Atlanta University Atlanta, Georgia 30314*

Abstract. We used a variety of picosecond transient and cw spectroscopies to investigate the linear and nonlinear optical properties of films of PPE/PPV copolymer semiconductor. The spectroscopies used include absorption, electro-absorption (EA) and two-photon-absorption (TPA). In addition to the odd parity excitons at ca. 3.0 eV, we also found a broad two-photon absorption band centered at about 4 eV, which is due to strongly coupled even parity excitons.

INTRODUCTION

π-conjugated semiconductor polymers have become important materials because of their potential applications as active media in organic light emitting diodes (OLED's) [1], and other optoelectronic devices, such as field effect transistors[2] and photovoltaic cells. Recently a PPE/PPV hybrid polymer has been successfully synthesized and was shown to be an excellent active medium for OLED applications [3]. This copolymer contains both PPE and PPV chromophores with a nearly perfect overlap between the emission band of the PPE chromophores and the absorption band of the PPV chromophores that leads to a very efficient energy migration from PPE to PPV excited states. We have already studied and reported the photoexcitation dynamics and laser action in solutions and thin films of PPE-PPV copolymer using a variety of ultrafast and steady-state spectroscopy techniques [4]. Those studies are considered to be the first laser action reported in PPE-type polymers. In the present paper we report our studies concerning the even parity excited states of PPE/PPV copolymer.

EXPERIMENT

The two-photon absorption (TPA) spectrum was measured using the pump-probe correlation technique. The pump beam (from a homemade Ti-Sapphire regenerative amplifier) was set at 1.55 eV, below the copolymer absorption band, whereas the probe beam (from a super-continuum generated in a sapphire crystal) covers the spectral range from 1.5 to 2.6 eV. The temporal and special overlap between the pump and probe beams leads to a photoinduced absorption (PA) signal that peaks at t = 0. This PA has a temporal profile similar to the cross-correlation function of the pump and probe pulses, which we interpret here as due to TPA of one pump and one probe photons.

For the electro-absorption (EA) measurements, the light source was derived from a Xe lamp, with broadband visible and ultraviolet spectral range. The light was dispersed through a monochromator, focused on the sample, and detected by a UV-enhanced silicon photodiode. A small sine-wave source was connected to a custom-built transformer, the output of which was connected to the electrode (40 μm spacing). The electrode was placed in a cryostat for low temperature measurements. For each EA spectrum, the transmission (T) was measured with a mechanical chopper while the electric field was turned off. The differential transmission (ΔT) was measured without the chopper, with the electric field on, and with the lock-in amplifier set at twice (2f) the electric field modulation frequency, f.

CP772, *Physics of Semiconductors: 27th International Conference on the Physics of Semiconductors,*
edited by José Menéndez and Chris G. Van de Walle
© 2005 American Institute of Physics 0-7354-0257-4/05/$22.50

RESULTS AND DISCUSSION

The room-temperature optical absorption spectrum of the PPE/PPV copolymer film is shown in the inset of the Fig. 1. Figure.1 shows the TPA spectrum of a PPE-PPV free-standing film. It is seen that the threshold of the TPA spectrum is blue-shifted respect to that of the linear absorption. The TPA spectrum also displays a peak at about 4eV, which is consistent with a similar spectral feature found in the EA spectrum (Fig. 2). As is well known, most of semiconductor polymers belong to the C_{2h} symmetry group. In this case the excited energy states in the correlated electron picture belong to A_g (even) or B_u (odd) irreducible representations. The ground state is obviously $1A_g$. For the C_{2h} symmetry group a one-photon transition is electric dipole allowed between A_g and B_u states. Consequently even parity excitons (A_g) are forbidden in linear absorption, but become allowed in a two-photon absorption process, which is a $\chi^{(3)}$ non-linear optical process. It follows that strong resonances in the TPA spectrum peak at A_g excited states. We thus can assign the strong TPA band at 4eV to the two-photon allowed mA_g state, which is about 0.8eV above the lowest, $1B_u$ exciton energy.

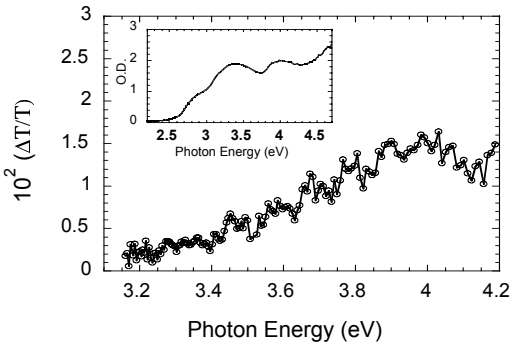

FIGURE 1. Two-photon absorption spectrum of a PPE/PPV film. The inset shows the linear absorption spectrum.

Figure. 2 shows the PPE/PPV EA spectrum. Below 4eV the EA spectrum is composed of strong features in the range of band I in the linear absorption spectrum. It exhibits a derivative-like feature with zero crossing at 2.97eV. In addition, there are two vibrational satellites at 3.2eV and 3.7eV, respectively. These features are formed due to an electric field induced red-shift (Stark shift) of the $1B_u$ exciton and its phonon sidebands. In addition to the Stark shift at low energy there is an electric field induced absorption band at 4.17eV. In agreement with the TPA spectrum we assigned this EA band to the mA_g exciton absorption, which is forbidden in linear absorption. This state is observable in EA since the external electric field transfers some oscillator strength from the allowed $1A_g \rightarrow 1B_u$ transition to the $1A_g \rightarrow mA_g$ forbidden transition.

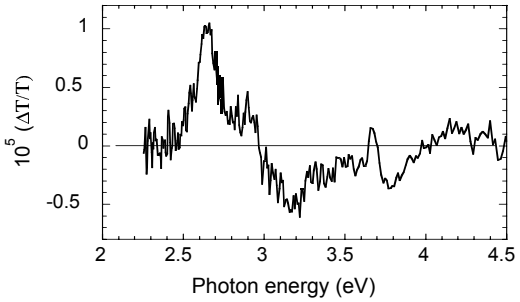

FIGURE 2. EA spectrum of PPE/PPV copolymer measured at 30K with field strength $F=5\times10^4$V/cm.

CONCLUSION

In this work we studied in films of PPE/PPV copolymer exciton states with even (A_g) and odd (B_u) parity using absorption, TPA and EA spectroscopies. From the EA spectrum we determined the $1B_u$ exciton to be at about 3 eV, following by two phonon side bands, and a strong mA_g state at ≈ 4 eV, about 1 eV above the $1B_u$ state.

ACKNOWLEDGMENTS

At the University of Utah this work was supported in part by NSF-DMR Grant No. 02-02790 and DOE Grant No. 02-04ER46109. The work at Clark Atlanta University was supported in part by the Air Force Grant No. F49620-00-1-0090.

REFERENCES

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature* (London) **347**, 539 (1990)

2 Y. Yang and A. J. Heeger, *Nature* (London) **372**, 344 (1994).

3. Q. Chu, Y. Pang, L. Ding, and F. E. Karasz, *Macromolecules* **36**, 3848 (2003).

4. M. Tong, C. X. Sheng, C .Yang, Z.V.Vardeny, and Y. Pang, *Phys. Rev. B* **69**, 155211 (2004) .

Copyright of AIP Conference Proceedings is the property of American Institute of Physics. The copyright in an individual article may be maintained by the author in certain cases. Content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.